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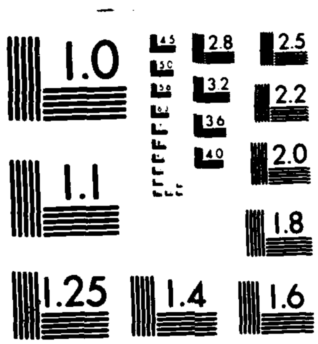

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ION FORMATION FROM ORGANIC SOLIDS
R.J. COLTON Naval Research Laboratory, Washington, DC 20375
4 February 1983

BRANCH OFFICE LONDON ENGLAND

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The second international workshop on Ion Formation From Organic Solids provided a general review of the field, and dealt specifically with ion formation processes and applications.

ION FORMATION FROM ORGANIC SOLIDS

The second international workshop on Ion Formation From Organic Solids (IFOS II) was held at the Physikalisches Institut der Universitat Münster, Münster, Federal Republic of Germany (FRG), from 7 through 9 September 1982. It was organized by A. Benninghoven and W. Sichtermann of the Univ. of Münster, and F. Saalfield and R. Colton of the Naval Research Laboratory, Washington, DC. Sponsors included the German Research Society (Deutsche Forschungsgemeinschaft) and the US Office of Naval Research.

In 1980, the first workshop brought together for the first time researchers in the areas of field desorption mass spectrometry (FDMS), laser desorption mass spectrometry (LDMS), plasma desorption mass spectrometry (PDMS), and secondary ion mass spectrometry (SIMS). (See *European Scientific Notes*, 35-1:1-3 [1981].) The original goals of the workshop were to examine experimental and theoretical questions concerning the formation of ions from organic solids, to explore the similarities between the new ionization methods for the study of nonvolatile organic solids, and to establish a dialogue between the active groups in the areas.

Since the first workshop, developments have increased rapidly, as evidenced by the growing number of publications, by the use of combined approaches (e.g., SIMS/PDMS), and most recently by the development of a new technique known as fast atom bombardment (FAB) or, in essence, liquid SIMS. (The name FAB is misleading because the nature of the regenerating liquid matrix, not the charge state of the primary beam, contributes to the ion formation process.)

Sixty scientists--up from 37 in 1980--attended the workshop; nine countries were represented. There were two participants from Austria and Sweden; one each from Canada, Japan, Liechtenstein, and the Netherlands; three from the UK; 16 from the US; and 33 from the FRG. The proceedings will be published by Springer-Verlag in early 1983.

Review Papers

The first day's program was largely tutorial, consisting of six invited review papers on FDMS, PDMS, LDMS, SIMS, FAB, and "Ion Emission From Liquids." The authors commented specifically on the following topics: (1) experimental setup, (2) sample preparation, (3) main features of the mass spectra, (4) desorption mechanism, (5) ion energy-angular distribution, (6) ion yield, and (7) influence of the physical-chemical environment. Several contributed papers and three panel discussions covering ion formation, instrumentation, and applications followed in the remaining 2 days.

F. Röllgen (Univ. of Bonn) presented the review paper on FDMS, the first technique to revolutionize the study of nonvolatile and thermally labile compounds. The main features of the mass spectra are characterized by intense $[M+H]^+$ or $[M+alkali]^+$ ions; M^+ molecular ions have been observed for more volatile molecules. Fragmentation is limited and known to vary with emitter preparation and temperature. Negative ion FD spectra show less fragmentation than the positive ion spectra. Röllgen discussed the types of additives used to enhance FDMS spectra. They include matrix

compounds such as polyvinyl alcohol and glycerol, which promote the solvation of ions; alkali salts such as LiI, NaI, and CsI, which increase the ionization efficiency by cationization; and acids such as tartaric acid or toluene sulfonic acid, which promote fragment ion formation. Röllgen also discussed ionization mechanisms involving field ionization, desolvation, and thermionic processes.

R. Macfarlane (Texas A&M Univ.) gave the review paper on PDMS, in which megaelectronvolt particles (from the fission of ^{252}Cf or from an accelerator) are the source of excitation. PDMS differs somewhat from the other techniques as its excitation process is electronic. However, PDMS does show strong spectral similarities with the other techniques in that M^+ and $[M+H]^+$ ions are emitted and cationization-anionization occurs. Other factors--such as sample preparation, physical-chemical environment, and matrix effects in PDMS--have not yet been explored, perhaps because of the time needed for data collection, typically more than 24 hours.

Macfarlane also pointed out that although not every incident particle causes an ion to be emitted, the average yield is still 3 to 6 ions per primary ion. The sampling times and sporadic yields make time-of-flight (TOF) instruments the analyzer of choice. Another active research area in PDMS addresses the question of how the electronic excitation changes into translational motion. Several groups have shown that ion emission is a collective process having a $(dE/dx)^2$ dependence.

F. Hillenkamp (Univ. of Frankfurt) presented the review on LDMS. He demonstrated the versatility of the tecnnique; all laser wavelengths can be used on bulk or thin substrates, with thick or thin films, and for large or small sampling areas. Ionization occurs mostly by alkali ion cationization, and higher ion yields are observed for polar molecules. Hillenkamp also discussed four emission mechanisms: thermal evaporation of neutrals followed by gas-phase ionization, thermal evaporation of ions (Saha-Langmuir), "true" nonthermal laser desorption, and laser-plasma generation (Saha-Eggert). He indicated that the "true" nonthermal laser desorption mechanism describes best the situation for LDMS of organic compounds (and is perhaps closely related to SIMS and FAB). Hillenkamp also reported a strong matrix effect in LDMS, observing competition between ions of mixtures. He concluded that quantitative analysis would be difficult, and as no theory currently exists, internal standards must be used. He attributed the spectral similarities between LDMS and the other techniques to similar "chemical effects."

A. Benninghoven presented the review paper on SIMS. He outlined the fundamental sputtering event as impact cascade in $<10^{-12}$s, implantation of primary species, and the emission of neutrals, + and - ions, electrons, and photons. The ion emission mechanism was also discussed in terms of the yet unanswered question of cluster or direct emission versus recombination. Benninghoven also described the influence on the emission of such parameters as surface coverage, primary species energy, pH, and adsorption site dependence. For the emission process, Benninghoven outlined a "precursor model," which has on the surface a

preformed ion that undergoes fast evaporation and charge sign conservation during sputtering. Species emitted from the high-energy region of the impact zone are expected to be fragmented. Benninghoven introduced the FAB technique by indicating that the important difference between FAB and fast ion bombardment (FIB) is that FAB uses a liquid matrix. The charge of the primary species has little or no effect.

C. Fenselau (Johns Hopkins Univ.), substituting for M. Barber, gave an excellent review of FAB. She described the characteristics of a good matrix, which must be relatively involatile and viscous, and must dissolve the sample. In addition, the likely role of the liquid matrix was to replenish the surface with solute molecules, to lower the desorption energy for the molecules by solvation and charge separation, and to create a preformed ion. Fenselau also indicated that while acidic matrices enhanced the $[M+H]^+$ ion yield (and positive ion spectra in general), nonacidic matrices were best for negative ion spectra. Additives such as salts and detergents also helped provide good ion yields. In addition, FAB is easy to use, provides a long-lasting signal, and has high mass sensitivity, e.g., insulin with m/z >6000. Four current mechanisms were also cited: sputtering from the surface, desolvation of ions in droplets, gas-phase chemical ionization, and a localized, nonequilibrium thermal process.

The last review paper was by M. Vestal (Univ. of Houston) on ion emission from liquids, a subject not previously covered. Vestal described a thermal spray apparatus that produces molecular ions directly from solution without an applied field or ionizing beam. Molecular ions are produced when solutions containing nonvolatile solutes are rapidly vaporized after flowing through a heated nozzle. The proposed ionization mechanism is similar to that known as spray electrification, in which droplets containing solvated ions are stripped of the solvent molecules. The flow rates in the apparatus are compatible for LC-MS applications.

The first day ended with two contributed papers. The first was by K. Busch (Purdue Univ.) on the internal energy effects of solvation in desorption ionization (DI). DI is a name coined by G. Cooks and Busch to describe all "soft" ionization techniques. Busch discussed the various types of solid and liquid matrices used in DI and their effects on the ionization process. For example, some matrices can control the internal energy of the desorbed ion. The second paper, by R. Cotter (Johns Hopkins Univ.), was on time-resolved laser desorption mass spectrometry. He described the sequence of events following a laser pulse: laser pulse occurs; substrate reaches maximum temperature; alkali ions, Na^+, are emitted; molecular ions, $[M+Na]^+$, are emitted; pyrolysis occurs.

Ion Formation

The second day of the workshop dealt with ion formation processes. The first paper was by H. Block (Fritz Haber Institute, Berlin) on laser-pulse-induced field desorption. He described how thermal activation in an applied field can increase ion yields. D. Hercules (Univ. of Pittsburgh) presented a paper on the mechanism of ion formation

in laser mass spectrometry of organic compounds. He described a model (using amino acids) in which intermolecular complexes form related $[M+R]^+$ and $[M-R]^-$ pairs of ions.

D. Greifendorf (Univ. of Münster) presented a paper on the secondary ion emission from C_2H_2 and C_2H_4 on Ni surfaces. D. Dück (Schott Ruhrglas) presented a paper on heavy ion induced desorption. He described the functional dependence of the charge state and energy of the incident ions. K. Wein (Univ. of Darmstadt) also talked about secondary ion emission by bombarding heavy ions with charge states up to 45. For monatomic ions, the ion intensity Y was proportional to the charge squared or cubed--i.e., $q^{2 \text{ or } 3}$; whereas for polyatomic ions, Y is proportional to q^o.

F. Kruger (Max-Planck-Institut, Heidelberg) compared ion formation with heavy ions, laser pulses, and dust particles. His results were interpreted as a nonequilibrium thermal process. The most intriguing result of his work dealt with the emission of ions during the bombardment of the target with dust particles that ranged in size from 0.1 to 15 μm. The next paper was by W. Lange (Univ. of Münster) on SIMS of ultrahigh vacuum amino acid layers deposited on metal surfaces. Intensity variations in the $[M+H]^+$ ions glycine on Au, Ag, and Cu surfaces were interpreted by the emission of ions from different adsorption sites on the surface. K. Standing (Manitoba Univ.) reported some TOF-SIMS measurements of the cluster ions of CsI. He showed that the large cluster ions $[Cs(CsI)_n]^+$ were metastable for n>7. W. Sichtermann (Univ. of Münster) discussed the temperature dependence of secondary ions emitted from phenylalanine on Ag. His results from SIMS and thermal desorption studies were interpreted by a model in which phenylalanine occupies two different adsorption sites on Ag. B. Sundquist (Univ. of Uppsala) talked about fast heavy ion induced desorption of small proteins; bovine insulin produced high mass ions at m/z 5742 + 5 (M^+) and 11447 + 15 ($2M^+$).

A panel discussion by the speakers who gave the review papers on ion formation was chaired by R. Honig (RCA Laboratories). The topics treated included primary beam (energy, flux density, angle, dosage, and charge); target character (preparation, surface properties, solid or liquid adsorption); energy transfer; charge transfer; secondary ion emission (charge/electronic state, energy distribution, angular distributions, time scale, and metastable decay); ion yield (matrix effects, alternate channels); and the emission model.

There were several contributed papers and a panel discussion dealing with instrumentation. The first paper was by H. Peters (Leybold-Heraeus) on a low cost SIMS for organic compounds. H. Wollnik (Bayer AG) discussed energy focusing in TOF-MS instruments. A paper by H. Heinen (Leybold-Heraeus) dealt with the LAMMA 1000 instrument, a new reflection mode laser microprobe mass analyzer, and its application to ethylene diamine tetraaceticacid (EDTA) and diolen. The final paper of the session was given by P. Steffens (Univ. of Münster) on the design and performance of a new multiple-focusing TOF instrument for SIMS. The instrument boasts a high mass range (up to 5000 amu), a pulsed primary beam, and a high detection

efficiency provided by post acceleration. The instrumentation panel chaired by J. Wyatt (Naval Research Laboratory) consisted of Cotter, M. Story (Finnigan MAT), Wollnik, Steffens, and Macfarlane. They discussed topics such as transient recorders versus pulse counting in TOF detection systems and ways to make ions live longer. The panel also discussed whether it is necessary to have a higher mass range and higher resolution.

Applications

The last day, devoted to applications, began with three papers on SIMS of polymers. The first was by R. Colton (Naval Research Laboratory) on the SIMS of polymers and of organic adsorbates on carbon. He presented results on polystyrene (with ion and neutral bombardment) and polyalkyl-methacrylates. Various polycyclic aromatic compounds were also analyzed directly from the surfaces of carbon particles and of liquid metals (Ga) using dynamic primary ion beams. The second polymer paper, by D. Briggs (ICI), was about the practical problems associated with the analysis of insulators, i.e., charge neutralization, electron stimulated desorption, and damage rate. The third polymer paper, by A. Brown (Univ. of Manchester), compared the SIMS and FAB spectra of polymeric materials. Although the spectral results were nearly identical, the FAB experiment gave minimal charging and five times the sensitivity.

A paper by P. Wieser (Univ. of Hohenheim) described experiments on laser-induced cationization of saccharides. His results were comparable to SIMS and FAB of saccharides. U. Seydel (Forschungsinstitut Borstel) presented a paper on tracing bioorganic molecules in plant tissue with LAMMA; he identified a lipid at m/z 1890. F. Heresh (Univ. of Vienna) discussed the thermal processes in repetitive laser desorption mass spectrometry. He also observed high molecular weight saccharides in his experiment. Dr. H. Jungclas (Univ. of Marburg) discussed problems in the standardization of ^{252}Cf-plasma desorption mass spectrometry. He described spectral changes related to sample thickness, sample impurity levels, secondary ion acceleration potential, ion beam divergence, and secondary ion detection. J. Campana (Naval Research Laboratory) discussed ion abundance calibrants and high mass reference standards in SIMS and FAB. He described the use of alkali halide (NaI and CsI) cluster ions to calibrate mass spectra and quadrupole mass spectrometers. Using a magnetic sector FAB instrument, Campana also observed cluster ions of $[Cs(CsI)_{99}]^+$ at m/z 25,854.

H. Kambara (Hitachi Ltd.) detailed the changes that occur in the secondary ion and daughter ion mass spectral patterns for some biological compounds as a function of various experimental conditions. M. Junack (Univ. of Münster) also described some biological and medical applications of organic SIMS.

The afternoon session on applications began with a paper by F. Field (Rockefeller Univ.) on an FAB study of the mass spectra and radiation chemistry of glycerol. He found that particle bombardment of glycerol produced many new species and that ∿100 glycerol molecules are converted (damaged) per incident atom. U. Rapp (Finnigan MAT) presented some FAB applications in which he used voltage scanning to determine exact

masses. C. Costello (MIT) discussed the practical applications of FAB in biochemistry. She described the analysis of peptides. W. Aberth (Univ. of California) also discussed SIMS of bio-organic compounds and described a new Cs^+ ion source that was only 2.7-cm long.

The session ended with a panel discussion of future developments in applications. The panel, chaired by F. Saalfeld (Naval Research Laboratory, now Office of Naval Research, Arlington, VA) consisted of Hercules, Honig, Rapp, and Jungclas. The topics included high mass limits, detection limits, quantification, combined methods, spectral reproducibility, spectral reliability, small area analysis, and the detection and ionization of emitted neutrals.

In summary, all participants agreed that the workshop provided an excellent forum for discussing new ideas and planning new experiments. I believe that the progress made in the first and second workshops has already contributed to the development of new mass spectrometric techniques.

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